CHEMILUMINESCENCE FROM ATMOSPHERIC GAS REACTIONS

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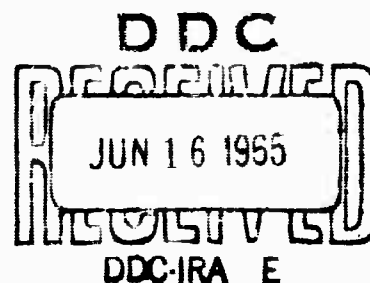
Electro-Dynamics Laboratories

Departments of Chemistry and Electrical Engineering

UTAH STATE UNIVERSITY

Logan, Utah

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FINAL REPORT

Contract No. AF19(628)-3821

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ABSTRACT

Chemical reactions involving active nitrogen and oxides of nitrogen have been studied with the relatively new technique of infrared chemiluminescence. Spectra have been obtained and presented of the N + NO reaction from 1 to 6 microns. First overtone emissions of nitric oxide at 2. 7 microns have been obtained from the reaction of N + NO_2 and the intensity variations studied as a function of NO_2 concentration. Equilibrium between the vibrational and rotational modes has not been achieved. The rotational temperature is only several hundred degrees, whereas the vibrational temperature is several thousand degrees. This reaction shows similarities to the H + Cl_2 reaction studied by Polanyi [1, 2]. In addition to energy transfer information, this reaction shows that infrared chemiluminescence can yield valuable information about the mechanism of complex chemical reactions.

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INTRODUCTION

Detailed knowledge of the chemical kinetics, energy transfer processes and radiative processes therein is of fundamental importance and urgently needed for an understanding of the behavior of the upper atmosphere. Very little is known about the radiative processes in the normal upper atmosphere, and practically nothing is extant about radiative phenomena following high altitude nuclear explosions. The technique of infrared chemiluminescence has been found to be a most valuable tool for investigations of this kind, and experiments indicate that infrared emission spectra can indeed lead to a detailed understanding of many mechanisms.

Some of the major constituents of the upper atmosphere are O, O_2, N, N_2, NO, and O_3. The reactions of interest among these constituents are the following:

$$(1) \quad N + O_2 \rightarrow NO + O$$

$$(2) \quad N + O + (M) \rightarrow NO + (M)$$

$$(3) \quad N + O_3 \rightarrow NO + O_2$$

$$(4) \quad O + NO \rightarrow NO_2$$

$$(5) \quad O + NO + (M) \rightarrow NO_2 + (M)$$

$$(6) \quad NO + O_3 \rightarrow NO_2 + O_2$$

$$(7) \quad O + NO_2 \rightarrow NO + O_2$$

$$(8) \quad N + NO \rightarrow N_2 + O$$

$$(9) \quad N + NO_2 \rightarrow N_2O + O$$

$$(10) \quad N + NO_2 \rightarrow NO + NO$$

$$(11) \quad N + NO_2 \rightarrow N_2 + O_2$$

$$(12) \quad NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$(13) \quad NO + NO_2 \rightarrow N_2O_3$$
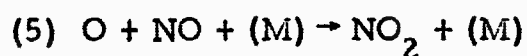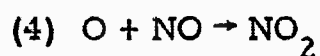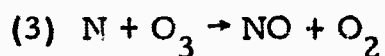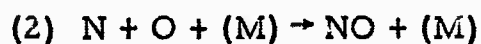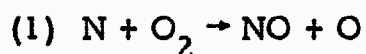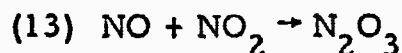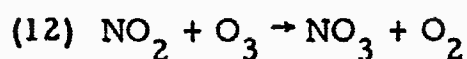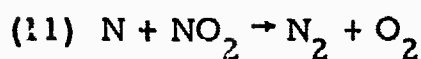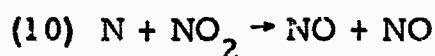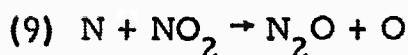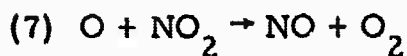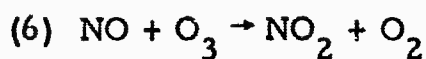
All of these reactions are exothermic. Reactions (2), (3), (4), (5) and (6) are known to be at least visibly chemiluminescent, and all except (8) and (11) are expected to be chemiluminescent in the infrared. Reactions (8) and (11), the products of which have no dipole moments for infrared emission, are both highly exothermic and probably produce N_2 and O_2 in highly excited vibrational states. Vibrational-vibrational energy transfer between these and polar molecules may then occur, leading to infrared vibraluminescence.

The reactions listed have widely varying rate constants (Table 1), but until more is known about the distribution of the exothermic energy among the degrees of freedom of the products, the dipole moments of the products and their collision lifetimes, it will be impossible to determine their true chemiluminescence efficiencies. It is conceivable that some of the slower reactions may be major contributors to the

infrared emission from the nitrogen-oxygen system. The survey work conducted in this laboratory indicates that the products of many of the reactions listed emit very brightly in the infrared.

EXPERIMENTAL

The determination of the absolute efficiencies described above
is an extremely difficult problem and requires highly sophisticated
techniques. The principal problems to be overcome are the following:

(i) Concentrations and flow rates of the reactants and products
must be measured very accurately. Particular care must be taken to
measure the concentrations of atomic species with precision.

(ii) Reactions must be studied at low pressures (10^{-2} to 10^{-3} torr)
to minimize collisional deactivation and vibrational equilibration of
excited species and simulate upper atmospheric conditions.

(iii) High flow velocities must be achieved to minimize the "residence
time" of individual atoms and molecules in the reaction cell. In this
manner, reaction cell wall effects are made nearly negligible, and
vibrational equilibration and collisional deactivation effects are further
reduced.

(iv) Radiometric and high resolution spectrometric measurements
must be made with extremely sensitive well-calibrated instruments.
A fairly good signal-to-noise ratio is desirable in all measurements so
that a high degree of confidence may be had in the chemiluminescent
efficiencies ultimately determined.

The problems described above define only in a general manner the careful measurements that must be made. It should be noted, however, that there are a multitude of smaller but related problems that must be contended with in a truly definitive study of this type. For example, not all of the reactions listed can be studied using the same experimental techniques; atom-molecule and molecule-molecule reactions are studied using significatnly different methods, and some reactions must be run at very high temperatures to acquire the needed information.

Much has been done and more must be done to satisfy the above requirements. Techniques have been developed and equipment has been purchased, or designed and constructed when necessary, to increase the capabilities of this laboratory in the field of infrared chemiluminescence. Some of these will be described briefly here.

Two different flow-measuring instruments have been acquired, calibrated, and put to use. One is the Fischer and Porter tri-flat variable area flowmeter which measures flow rates of fluids by comparing their hydrodynamic forces with the net buoyed weight of a float. The other flowmeter measures the differential pressures across a conductance-limiting capillary. Titration techniques for measurement of O-atom and N-atom concentrations have been perfected, and an isothermal calorimetric detector has been designed to allow an independent measurement of free radical concentrations. This detector consists

of a wire coated with a suitable catalyst for atom recombination, and atom concentrations are calculated from the heat liberated when the detector is operated under isothermal conditions.

It has been found highly advantageous to use an infrared integrating sphere for the reaction cell. Much effort was expended to develop a sphere for the infrared whose performance agreed with theory. Several spheres were designed and built, installed in the chemiluminescence system, and found to have a gain of at least 20 in light-gathering power over more conventional types of reaction cells. The measured gain for an isotropic point source radiating inside the sphere agreed very well with theoretical predictions. Ultimately, a volume gain on the order of 50 is expected. However, the energy gain of the integrating sphere is not its sole advantage. Equally important is the fact that its efficiency is nearly independent of source position, thus allowing one to measure fairly accurately the total amount of energy radiated per unit time in a well-defined volume, regardless of source geometry or spatial uniformity.

A fast-flow system has been designed and installed; an Heraeus DK180 mechanical pump, with a pumping speed of 50 liters/sec in the viscous flow region, provides reaction cell residence times lower than 10^{-1} sec at roughly 5×10^{-2} torr and higher. For experiments at lower pressures the feasibility of using cryosorptive pumping has been

studied, and it appears that this technique could be employed success-
fully for work in the nitrogen-oxygen system. A large zeolite cryosorp ion
pump with a speed of 1000 liters/sec at 10^{-3} torr has been designed.
Its high speed would allow for the use of large reaction cells while
maintaining short residence times, thus providing reasonable signal-
to-noise within the desired gas kinetics restrictions. The problem of
hydrocarbon impurities would also be eliminated.

Extensive use has been made of Fourier spectroscopy. Interfero-
meters used as spectrometers offer large gains in signal-to-noise over
conventional spectrometers. The "thruput" or acceptance $A\Omega$ of even
the simplest interferometer is relatively large, and the multiplex gain
of interferometers (i.e., looking at all wavelengths all of the time) is
considerable when studying a broad spectral region with fairly high
resolution. Initially, two Block Associates I-4 interferometers were
modified to drive to 10 cm^{-1} resolution with accessory fringe monitoring
for accurate determination of mirror position. Many spectra have
been studied successfully with these two relatively unsophisticated
Michelson-type instruments. A lamellar grating interferometer is
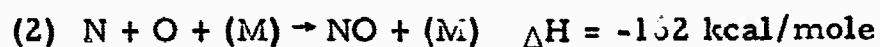also now available for studies at wavelengths of 15 microns and longer.

Lead sulphide, lead selenide, and indium antimonide detectors
have all been used with a large degree of success. Reliable dewars
have been built to permit economical and unattended operation of
detectors for periods of several hours.

Studies of reactions (3), (6), and (12) require that large quantities
of pure ozone be produced and stored economically and safely. An
ozonator has been designed and built and used for survey work; its
efficiency is nearly equal to that of the ozonators commercially available.
In the past, purification, storage, and handling of ozone has been
accomplished by liquefaction of O_3, O_2 mixtures, distillation, and
withdrawal of liquid samples of pure ozone. However, the handling of
ozone in its liquid state is a very dangerous proposition and has resulted
in violent explosions in many laboratories, causing damage to equipment
and injuries to personnel. The method developed by Kaufman and
Del Greco for gaseous ozone purification and storage has been adapted
for use in this laboratory. An O_2, O_3 gas mixture from the ozonator is
flowed through a trap containing silica gel cooled to -80° C, and the
ozone is selectively absorbed on the silica gel. This physical absorption
process is effective only for polar molecules; thus, the homopolar O_2
molecule easily flows through the trap. Utilizing this technique 5000
std. cc of ozone have easily been purified and stored for periods of
many hours.

DISCUSSION

Chemiluminescent phenomena occurring in the nitrogen-oxygen

reaction system are of great interest because of their probable

contributions to atmospheric radiation. The mechanism of NO production

in the atmosphere and its relation to infrared emission from NO is a

most important part of the problem.

Three reactions contributing to the production of NO under

different conditions (and at different altitudes) in the atmosphere are

(1) $N + O_2 \rightarrow NO + O$ $\Delta H = -44$ kcal/mole

(2) $N + O + (M) \rightarrow NO + (M)$ $\Delta H = -152$ kcal/mole

(3) $N + O_3 \rightarrow NO + O_2$ $\Delta H = -137$ kcal/mole.

At a pressure of 1 torr and a temperature of 300° K, reaction (3) is

approximately 1000 times faster than both reactions (1) and (2). However,

at higher temperatures and different pressures reactions (1) and (2)

can become quite important, and of course, the relative concentrations

of O, O_2, and O_3 in the atmosphere depend very critically on the

altitude. Therefore, the environment will, to a great extent, determine

the rate and method of production of NO and also the amount of energy

available for radiative processes.

Careful laboratory studies of reactions (1), (2), and (3) are extremely difficult for several reasons. Reaction (1) is so slow at room temperatures as to make it virtually impossible to study radiative phenomena associated with it, a fact confirmed by many experiments in this laboratory. Work has begun on apparatus which will make possible the study of this reaction at temperatures up to 1000° C. Infrared chemiluminescence studies of reactions (2) and (3) are complicated by the fact that NO production in these reactions initiates a chain of follow-on reactions (reactions (4) through (13)), none of which are entirely negligible either from a kinetics viewpoint or in terms of energy transfer. Because of this situation, the "modus operandi" has been to try to study each of these reactions individually and finally assess the importance of each to the complete system. In the following paragraphs, numbered by the reactions with which they are concerned, brief descriptions will be given of the status of this effort.

(1) $N + O_2 \rightarrow NO + O$
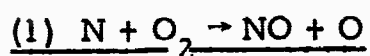
Several attempts have been made to study infrared emission from this reaction run at room temperature. Signal-to-noise ratios of less than unity have made it impossible to obtain spectral data of any significance. The principal effect observed has been the quenching of the nitrogen afterglow by molecular oxygen.

(2) N + O + (M) → NO + (M)
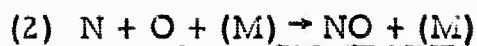
No attempt has yet been made to study this reaction directly because
of the complexity that would result from having N, O, O_2, O_3, and NO
all present simultaneously.

(3) N + O_3 → NO + O_2
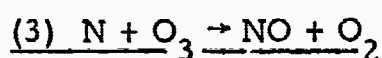
This reaction, although complicated considerably by follow-on
reactions, has been studied in some depth. It appears that NO is produced
in this reaction highly vibrationally excited, and infrared emission has
easily been observed.

(4), (5) NO + O + (M) → NO_2 + (M)

The visible chemiluminescence from this reaction is the well-known
"air afterglow." The recombination and the accompanying visible emission
have been studied in many laboratories. However, despite its apparent
simplicity there remains serious disagreement about the molecularity of
this reaction.

The spectral distribution of the continuum, previously determined
from 4000 A to 1.2 microns, has been measured to beyond 3.5 microns.
Infrared emission has been observed from vibrational states of NO_2 and
NO, the NO_2 ng formed vibrationally excited in the reaction. The NO
emission is primarily attributed to excitation by dissociation of NO_2
following the recombination or electronic-vibrational transfer from

$O_2(^1\Delta_g)$. The intensity of the vibrational emission relative to the continuum is pressure-dependent due to the considerably different radiative and collision lifetimes of the electronic and vibrational states of NO_2. It appears that at altitudes above 90 km more quanta of energy will be radiated in the infrared than in the visible.

(6) $NO + O_3 \rightarrow NO_2 + O_2$
(12) $NO_2 + O_3 \rightarrow NO_3 + O_2$
(13) $NO + NO_2 \rightarrow N_2O_3$
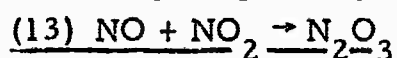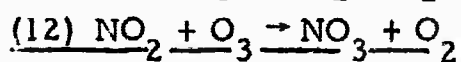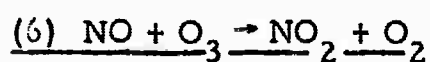
Reactions (6), (12), and (13) have not yet been studied directly because such studies require significantly different experimental techniques than those now in use. However, reaction (6) has been studied indirectly as a step following reaction (3). Very little is known about reactions (12) and (13), but they may ultimately aid in explaining several strong unidentified bands which have been observed.

(7) $O + NO_2 \rightarrow NO + O_2$
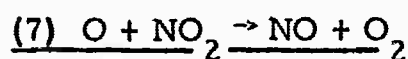
NO produced in this reaction does not appear to be highly vibrationally excited, and strong infrared emission has not been observed. Ther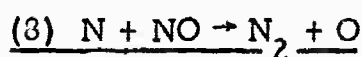e is evidence that the product O_2 molecule is highly vibrationally excited, but, of course, it has no dipole moment for infrared emission.

(8) $N + NO \rightarrow N_2 + O$

Fairly intense infrared emission was observed from reaction (8) and the follow-on reactions occurring with it. The accompanying spectra,

Figures 1 and 2, show the bands observed at 2.2, 2.7, 2.9, 4.5, and

5.4 microns; the 5.4 and 2.7-micron bands are attributed to fundamental

and first overtone of NO and the strongest band near 4.5 microns appears

to be the ν_3 fundamental of N_2O. The weaker band near 4.5 microns is

still unidentified, as are the bands at 2.9 and 2.2 microns.

(9), (10), (11) $N + NO_2 \rightarrow N_2O + O + NO + N_2 + O_2$
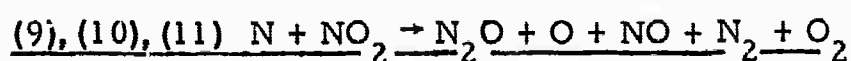
Much attention was devoted to the reaction of active nitrogen with

nitrogen dioxide, because nitrous oxide (N_2O) was unexpectedly found to

be the major radiator in many systems, and reaction (9) appears to be

the most probable source of N_2O. Several emission bands were observed

in the survey, located near 2.7, 2.9, and 3.2 microns. Many experiments

were performed on the reaction varying all the possible parameters to

achieve maximum intensity of the 2.7-micron band which was quickly

identified as nitric oxide. It was not possible to take spectra with the

IR-8 on this reaction with the slits open less than 0.7 mm (spectral slit

width of 10 cm^{-1}). However, a partially resolved spectrum was obtained

[3] which could be correlated with first overtone transitions from upper

vibrational levels of the ground electronic state $2 \rightarrow 0$, $3 \rightarrow 1$, $4 \rightarrow 2$, and

$5 \rightarrow 3$. Maximum infrared chemiluminescence was produced immediately

after the final green glow of the reaction was obtained. Further addition

of nitrogen dioxide reduced the intensity of the emission. The emission
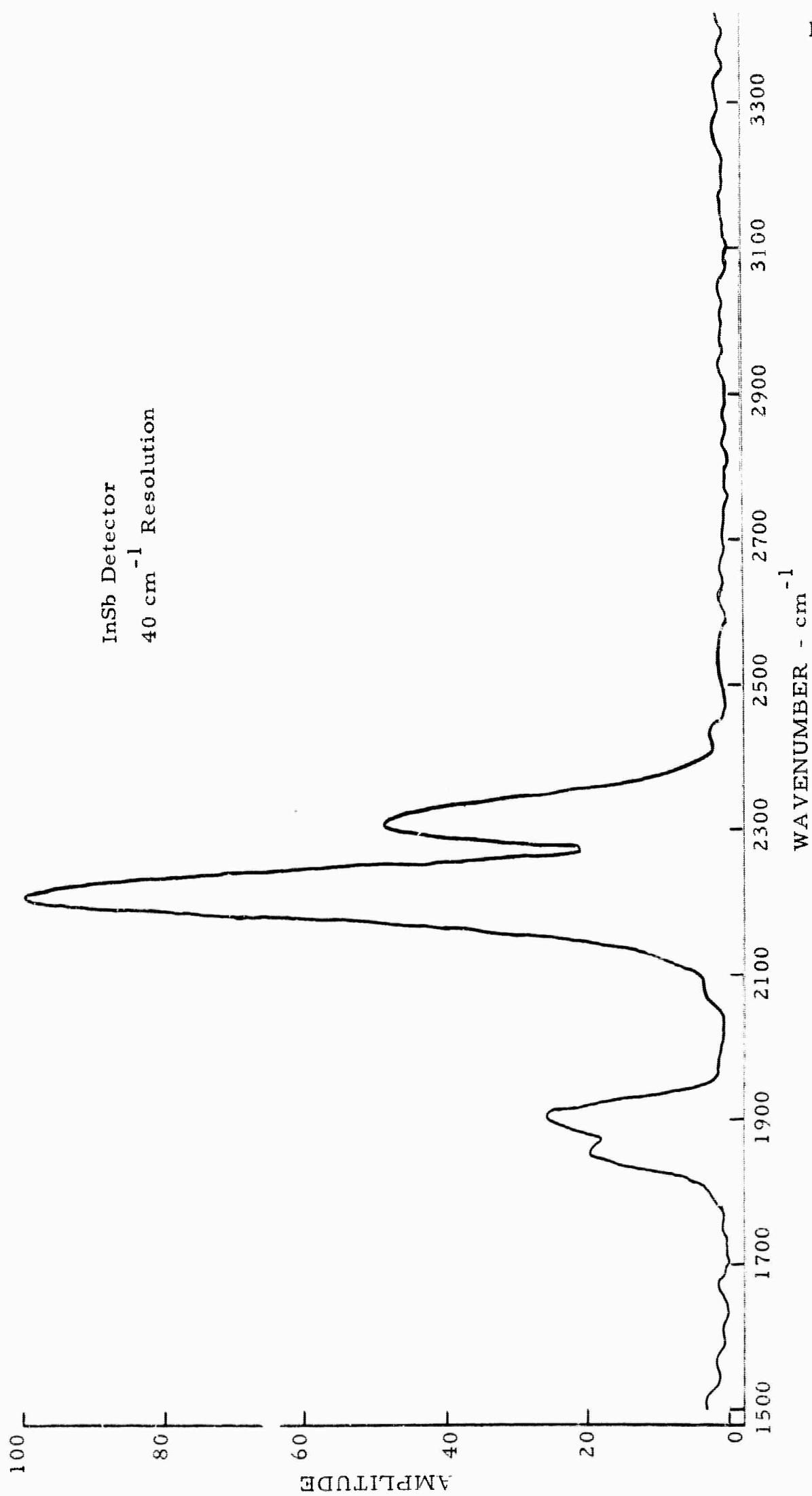
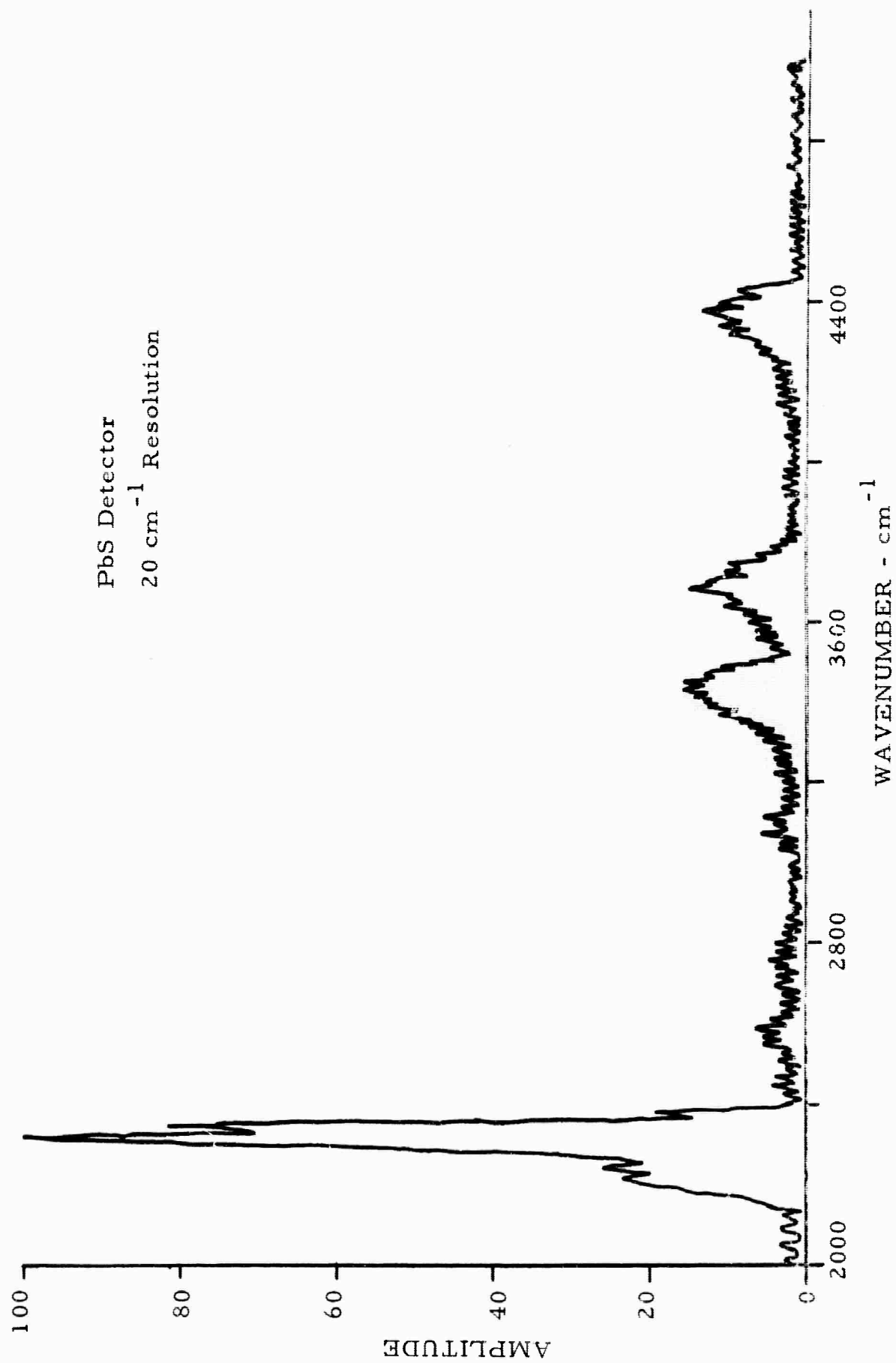Figure 1. N + NO reaction.

InSb Detector
40 cm^{-1} Resolution

Figure 2. N + NO reaction.

at 2. 9 μ has not been identified, but it has also been found in the reaction of active nitrogen with nitric oxide.

In conjunction with the studies on infrared chemiluminescence, a study was made of the emission spectrum of several gases which had been activated by a radio-frequency discharge. The spectra of methane, ethane and ketene were obtained [4]. The infrared emission of nitric oxide was studied as a function of cell pressure. Horn and Dickey [5] reported on such a study at pressures of 200 torr. Wilkinson, Price, and Mould [6] have also studied such emissions at relatively high pressures. Energy transfer is very rapid and quite normal emission spectra are obtained. At lower pressures ranging from 2 torr down to 10^{-3} torr, entirely different emissions are observed. Extremely sharp and strong peaks at 2. 75 and 2. 87 μ are produced along with some of the more normal emissions. These emissions may be due to ions and breakdown products from the discharge. Care must be taken in using this technique for spectroscopic studies of molecules.
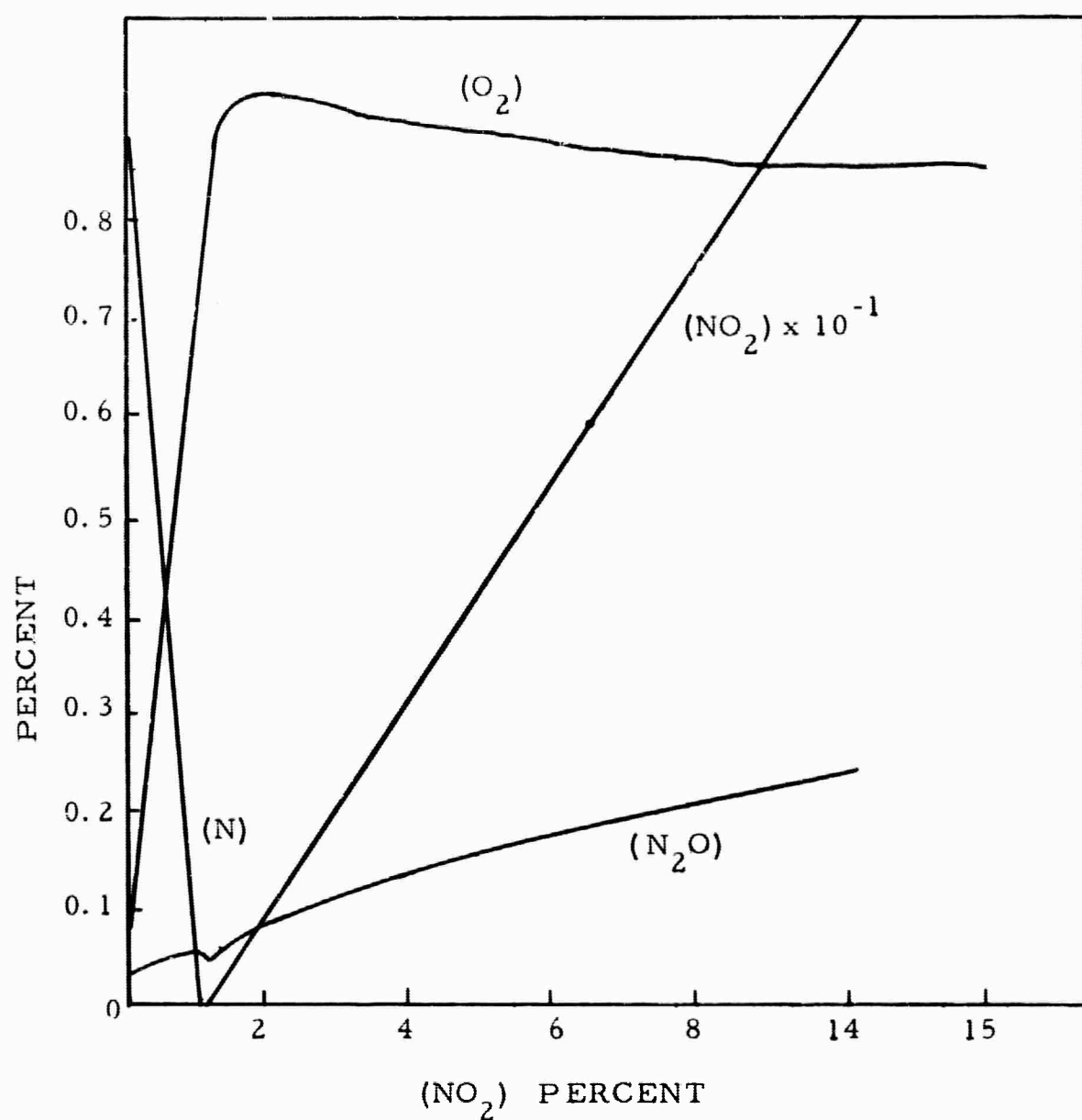
Figure 3. Reaction with nitrogen dioxide. The abscissas are the inflowing concentrations of nitrogen dioxide, the ordinates the steady-state concentrations in effluent gases.
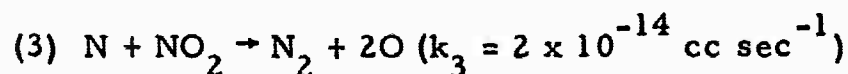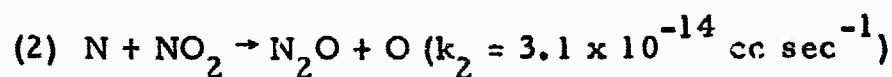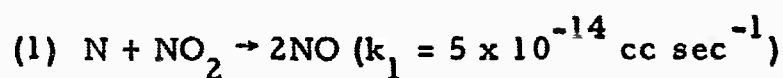
CONCLUSIONS

The studies on the infrared chemiluminescence resulting from the reactions of atoms with nitrogen oxides have yielded some interesting results concerning both energy transfer processes and chemical kinetics; these results have been presented [3]. In this section an exploration is made of the contribution of infrared chemiluminescence to the study of chemical reactions, particularly those which may occur in the upper atmosphere. Since a study of the reaction of active nitrogen with nitrogen dioxide has been one of the most thoroughly investigated, the discussion is based greatly on its results. This particular reaction is coincidently one of the most fascinating in terms of visible chemiluminescence, and it has attracted many well-known investigators.

Spealman and Rodebush [7] were among the first to note the color changes which occur when nitrogen dioxide is slowly introduced into a system containing active nitrogen, and Kaufman [8] has described the color changes in detail. Summarizing the chemiluminescence, active nitrogen produced by flowing nitrogen through an rf discharge gave the yellowish Lewis-Rayleigh afterglow which extended through the reaction cell to the cold trap. The introduction of nitrogen dioxide completely quenched this afterglow. Careful increases in the NO_2 flow rate produced

successively the blue nitric oxide glow and finally the yellowish-green

glow of excited nitrogen dioxide. Each glow was extinguished before the

succeeding luminescence appeared. In our experiments, the onset of

infrared chemiluminescence at 2.7 μ could be detected only at the

termination of the final yellowish-green glow. This infrared glow was

quenched by further increasing the nitrogen dioxide flow rate. Kaufman

found that the amount of NO_2 required to reach the initiation of the

yellowish-green glow was less than the amount of NO required to titrate

the same active nitrogen flow rate. The appearance of the yellowish-

green glow is the end-point for the titration of nitrogen atoms with nitric

oxide.

Several studies have been concerned with the reaction of nitrogen

atoms with nitrogen dioxide. Harteck and Dondes [9] were the first to

attempt a determination of the rate constant for the reaction. They

analyzed the products from the varying exposure of nitrogen oxides to

ionizing radiation. Their results were explained by the formulation of

three simultaneous reactions for nitrogen atoms and nitrogen dioxide.

(1) $N + NO_2 \rightarrow 2NO$ $(k_1 = 5 \times 10^{-14}$ cc sec$^{-1})$

(2) $N + NO_2 \rightarrow N_2O + O$ $(k_2 = 3.1 \times 10^{-14}$ cc sec$^{-1})$

(3) $N + NO_2 \rightarrow N_2 + 2O$ $(k_3 = 2 \times 10^{-14}$ cc sec$^{-1})$

During the same year, 19ˉ7, Kistiakowsky and Volpi [10] published a mass spectrometric study of the products from the reaction of active nitrogen with nitrogen dioxide. Nitrous oxide, oxygen, and nitrogen dioxide concentrations were determined in relation to the initial concentration of nitrogen dioxide. The data are reproduced in Figure 3. Although it was not possible to determine NO production, reactions (1), (2), and (3) were invoked to explain the results. The salient points of the results are that (1) O_2 production reaches a maximum at the N atom end ·point, while (2) the N_2O production passes through a minimum, and (3) NO was postulated to be present. Harteck and Dondes [11] published a critique of the results of Kistiakowsky and Volpi [10] , and they were able to explain the product ratios from the rate constants of their study [9]. However, they discounted a reaction scheme, shown in steps (4) and (5), that Kistiakowsky and Volpi proposed to convert NO into N_2O.

(4) $O + NO_2 \rightarrow NO^* + O_2$

(5) $NO^* + NO_2 \rightarrow N_2O + O_2$
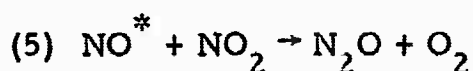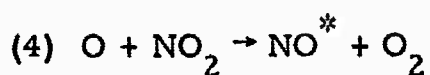
Chen and Taylor [12] studied the reaction of active nitrogen with ozone and used the rate constants of Harteck and Dondes [9] to explain their results. Although the primary process was

(6) $N + O_3 \rightarrow NO + O_2$
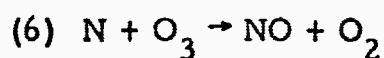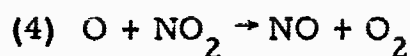
principally N_2O was found as product.

After 1960, published studies on the active nitrogen-nitrogen dioxide reaction seemed to ignore the rate constants for reactions (1) to (3) as determined by Harteck and Dondes. Verbeke and Winkler [13] found nitrous oxide to be the principal product from the reaction and invoked reaction (2) as the main process.

Clyne and Thrush have made studies of the reaction of nitrogen atoms with nitrogen dioxide [14] and oxygen atoms with nitrogen dioxide [15]. They made several assumptions about the reaction of nitrogen atoms with NO_2. They felt that:

(1) The initiation of the green nitrogen dioxide glow marked the complete removal of NO_2, NO, and N.

(2) The termination of the green glow marked the complete removal of oxygen atoms.

(3) The principal products of the primary process are nitrous oxide and oxygen atoms.

Their results show that the molecularity and ratio of rate constants are independent of temperature between 300 and 700° K. From the stated assumptions and careful flow measurements, they were able to evaluate relative rate constants for reactions (1), (2), and (3).

From their data

(1) $N + NO_2 \rightarrow 2NO$

(2) $N + NO_2 \rightarrow N_2O + O$

(3) $N + NO_2 \rightarrow N_2 + O_2$

(7) $N + NO \rightarrow N_2 + O$

(4) $O + NO_2 \rightarrow NO + O_2$
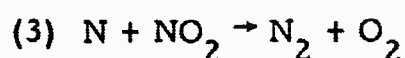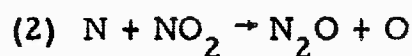
One nitrogen atom reacts completely with 0.83 NO_2 molecules, and 0.57 oxygen atoms are liberated at the first end-point where the green glow begins. Calculations based on these results give $k_2/k_1 = 4.7$, and $k_2/k_3 > 1.2$.

From the present study, it is apparent that the maximum NO concentration appears at the second end-point which is the disappearance of the green glow [3]. Nitric oxide molecules can be formed by reactions (1) and (4). In reaction (1) NO molecules are formed by making bonds and in (4) they are possibly formed by breaking bonds. It should be possible to study reaction (4) independently of (1), and this should be done. Polanyi has found that a small percentage of the total excess energy is located in the vibrational mode. However, the vibrational energy available is distributed principally to the newly formed bonds.

Clyne and Thrush [15] continued studies along this line by an investigation of the reaction of oxygen atoms with nitrogen dioxide, reaction (4). Oxygen atoms (mass 18) were reacted with $N^{16}O_2$.

Statistical scrambling of the oxygen in the products was observed by mass
spectroscopy. They concluded that a triangular transition state (I) was
formed rather than the linear transition state (II). These states are
indicated in Figure 4. Analogously, they felt that the reaction of nitrogen

O O   O O   O O   O   O
\ /   \ /   \ /   \ /
 N   N   N   N   N
 | / N |
 O   O   N

(I)   (II)   (III)   (IV)
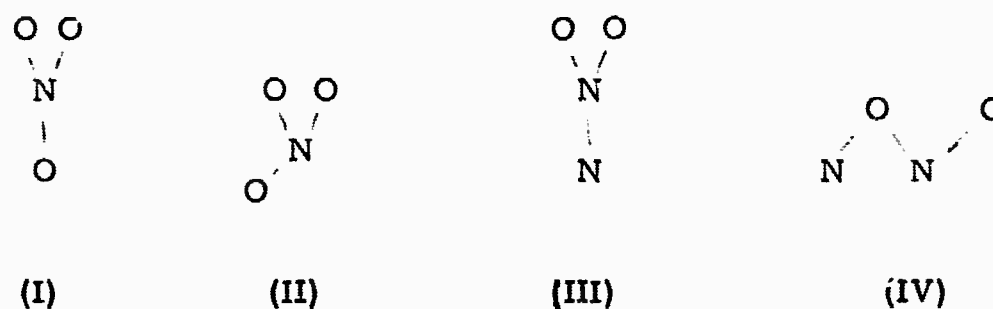
Figure 4. Nitrogen-oxygen transition states.

atoms with NO_2 must also go through a branched transition state (III).
A reaction proceeding through (I) could produce a newly formed NO bond
whereas (II) would not. A reaction proceeding either through (III) or (IV)
would have a newly formed NO bond. The nature of the transition state
has been debated and discussed by Benson [16] and Thrush [17].
Continued infrared chemiluminescence studies could possibly contribute
to a proper understanding of both transition states and the mechanism.

Table 1. Rate constants for nitrogen oxide reactions.

Reaction	Rate Constant (cc/sec)	Reference
$N + NO_2 \rightarrow 2NO\ (k_1)$	5×10^{-14}	[9]
	$k_2/k_1 = 4.7$	[14]
$N + NO_2 \rightarrow N_2O + O\ (k_2)$	3.1×10^{-14}	[9]
	10^{-14}	[10]
$N + NO_2 \rightarrow N_2 + O_2\ (k_3)$	2×10^{-14}	[9]
	$k_2/k_1 > 1.2$	[14]
$O + NO_2 \rightarrow NO + O_2$	3.5×10^{-12}	[19]
	2.1×10^{-12}	[20]
	1.7×10^{-12}	[21]
$NO + NO_2 \rightarrow N_2O + O_2$		
$N + O_3 \rightarrow NO + O_2$	5.7×10^{-13}	[20]
	1.7×10^{-14}	[12]
$N + NO \rightarrow N_2 + O$	2.2×10^{-11}	[20]
	4×10^{-11}	[22]
	$> 10^{-12}$	[21]
$NO + O \rightarrow NO_2 + h\gamma$	6.4×10^{-17}	[23]
	2.5×10^{-17}	[24]
$N + O + M \rightarrow NO + M + h\gamma$	5×10^{-33}	[25]

Table 2. Selected rate constants for atmospheric reactions.
(D.C. Sparks, M.H. Bortner, and K.S.W. Champion)

Reaction	Rate Constant (cc/sec)
Two Body Atom Recombination:	
1. $O + O \rightarrow O_2$	1×10^{-21}
2. $O + O_2 \rightarrow O_3$	1×10^{-21}
3. $O + N \rightarrow NO$	2×10^{-17}
4. $O + N_2 \rightarrow N_2O$	1×10^{-21}
5. $O + NO \rightarrow NO_2$	6.4×10^{-17}
6. $N + N \rightarrow N_2$	1×10^{-21}
7. $N + O_2 \rightarrow NO_2$	1×10^{-22}
8. $N + NO \rightarrow N_2O$	1×10^{-22}
Three Body Atom Recombination:	
1. $O + O + M \rightarrow O_2 + M$	$2 \times 10^{-31}\ T^{-\frac{1}{2}}$ (M = 0) $5 \times 10^{-32}\ T^{-\frac{1}{2}}$ (Other)
2. $O + O_2 + M \rightarrow O_3 + M$	3.2×10^{-35} exp (+900/T) (M = O_2) 2.6×10^{-35} exp (+900/T) (M = N_2) 6.5×10^{-34}
3. $O + N + M \rightarrow NO + M$	$2 \times 10^{-31}\ T^{-\frac{1}{2}}$
4. $O + N_2 + M \rightarrow N_2O + M$	2×10^{-33} exp (-10000/T)
5. $O + NO + M \rightarrow NO_2 + M$	3×10^{-33} exp (+900/T) (M = O_2) 4.5×10^{-33} exp (+900/T) (M = N_2)

Table 2. Continued.

Reaction	Rate Constant (cc/sec)
6. $N + N + M \rightarrow N_2 + M$	$6 \times 10^{-30} T^{-1}$
7. $N + O_2 + M \rightarrow NO_2 + M$	$1 \times 10^{-33} \exp(-3000/T)$
8. $N + NO + M \rightarrow N_2O + M$	$1 \times 10^{-33} \exp(-10000/T)$

Neutral Rearrangement

| Reaction	Rate Constant
1. $O + N_2 \rightarrow NO + N$	$1 \times 10^{-11} \exp(-38000/T)$
2. $O + NO \rightarrow O_2 + N$	$7 \times 10^{-17} T^{3/2} \exp(-19000/T)$
3. $O + NO_2 \rightarrow NO + O_2$	$3 \times 10^{-11} \exp(-530/T)$
4. $O + N_2O \rightarrow NO + NO$	$2 \times 10^{-10} \exp(-14000/T)$
5. $O + N_2O \rightarrow O_2 + N_2$	$5 \times 10^{-11} \exp(-14000/T)$
6. $O + O_3 \rightarrow O_2 + O_2$	$5 \times 10^{-10} \exp(-2800/T)$
7. $N + O_2 \rightarrow NO + O$	$3 \times 10^{-16} T^{3/2} \exp(-3300/T)$
8. $N + NO \rightarrow N_2 + O$	2.5×10^{-11}
9. $N + NO_2 \rightarrow N_2 + O_2$	$2 \times 10^{-13} \exp(-7000/T)$
10. $N + NO_2 \rightarrow NO + NO$	4×10^{-12}
11. $N + NO_2 \rightarrow N_2O + O$	1.6×10^{-11}
12. $NO + O_3 \rightarrow NO_2 + O_2$	$8 \times 10^{-13} \exp(-1200/T)$
13. $NO + O_2 + NO \rightarrow NO_2 + NO_2$	$1 \times 10^{-40} \exp(-4000/T)$

Table 2. Continued.

Reaction	Rate Constant (cc/sec)

Photo Dissociation

1. $O_2 + h\nu \rightarrow O + O$

2. $NO + h\nu \rightarrow N + O$

3. $NO_2 + h\nu \rightarrow NO + O$

4. $N_2O + h\nu \rightarrow N_2 + O$

5. $N_2O + h\nu \rightarrow NO + N$

6. $O_3 + h\nu \rightarrow O + O_2$

APPENDIX

The Reaction Cell

Several designs have been used for the reaction cell. The design has in general been governed by the need for maximum efficiency of collecting the optical radiation. Modified white cells and spherical reflector cells have both been tried. The white cell design suffers from the corrosive nature of most gas reactions, and expensive optics need to be resurfaced frequently. For part of the survey study a long cylindrical cell design proved useful in regular gas phase flow reaction studies. The radiation is collected as a colliminated beam traveling axially through the cell. Observation of wall reactions are minimized in this design, and molecules can be observed for relatively long periods of time before exhausting from the system. Also, the internal optical components are few and very simple. The most serious disadvantage of this type of cell is the large exit aperture which is often necessary. Typical cell arrangements are shown in Figure 5. Secondary gas ports can be added easily on small cells of this design.
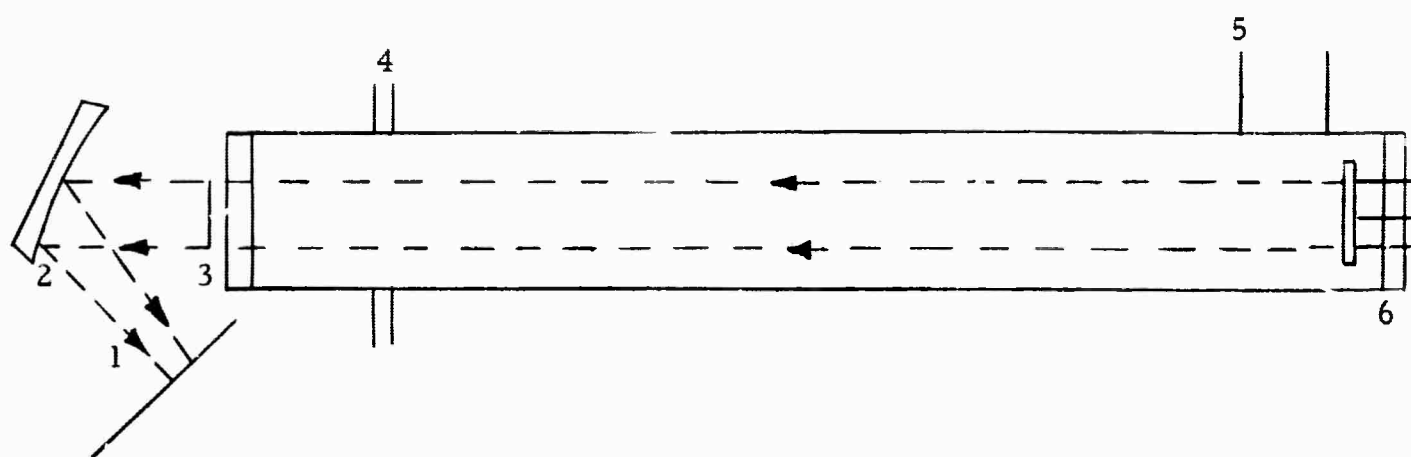
1. Entrance slit to monochromator
2. Collecting mirror for radiation
3. Window of reaction cell
4. Gas ports to cell
5. Exhaust from cell
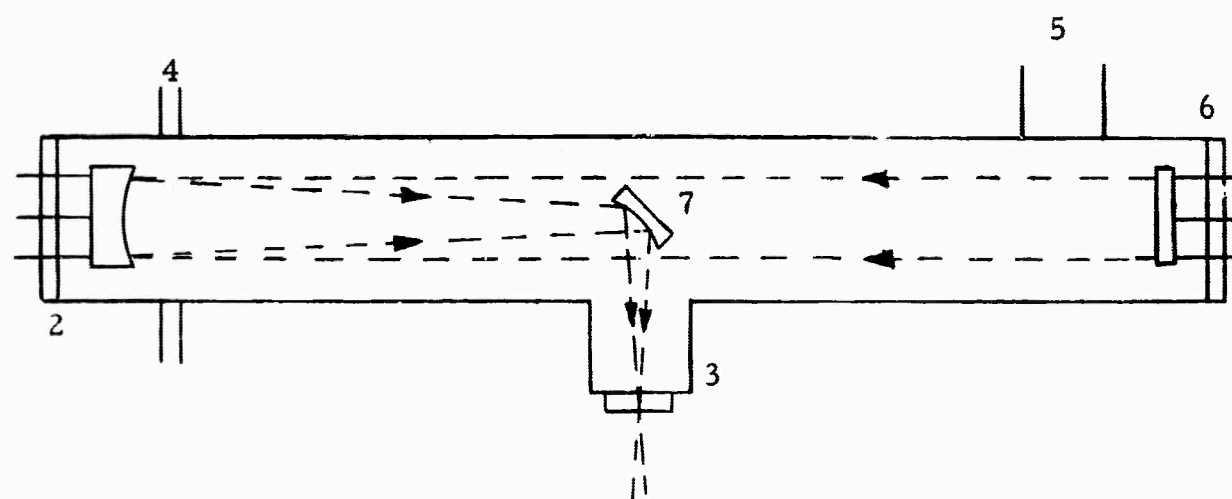6. Plane mirror
7. Small plane mirror

Figure 5. Reaction cell design.

Optical Spectrum Analyzers

Infrared chemiluminescence poses a problem long familiar to experimenters conducting far infrared absorption studies [18]. The intensity of the radiation is usually very weak so a high light gathering efficiency is mandatory. In addition, the radiation source for chemiluminescence is diffuse. Optical spectrum analyzers of high throughput $A\Omega$ have been required. Both interferometers and large monochromators have been used to good advantage in these studies. For the survey work and most of the studies, two instruments have provided inexpensive solutions. The Block I-4 interferometer has been used extensively and has proved to be extremely sensitive. Also, a Beckman IR-8 has been modified for an external source and detector.

Under separate funding Brower Laboratories, Inc., was commissioned to build a one-meter Czerny-Turner Monochromator with f/7 optics and 2-inch slits. The region from 1 to 9 microns is covered with 3 gratings operating only in the first order. A high light gathering efficiency is anticipated with this instrument, and a resolution of better than 5 A should be obtained with practical slit openings. The resolution for absorption work is about 2 A.

Signal-to-Noise Enhancement

Spectral resolution has so far been limited by the signal-to-noise ratio. Although the one-meter monochromator has not been thoroughly tested, minimum slit widths have been achieved in only one reaction with the Beckman IR-8. Therefore, additional techniques of improving S/N have been explored. Of the newly marketed signal averagers tested, the Technical Measurements Corporation CAT 1024 was found to be the most versatile and satisfactory instrument for real time spectra, whereas the Block Associates Coadder was found to be best for interferometric data.

Vacuum Pumping Systems (Cryosorption Pump)

Tests were made to determine the utility of a 1-kg cryosorption pump on loan from GCA Corporation. First a measurement was made of the minimum pressure which could be obtained at various flow-rates. Figure 6 shows the results of this test. Initially, the pump was evacuated and heated overnight. The pressure inside the pump reached a minimum of 10^{-3} torr. The pump was attached to an air flow system and pressure readings were taken on a pirani gauge for various flow rates. This test was completed in less than an hour so that the capacity of the
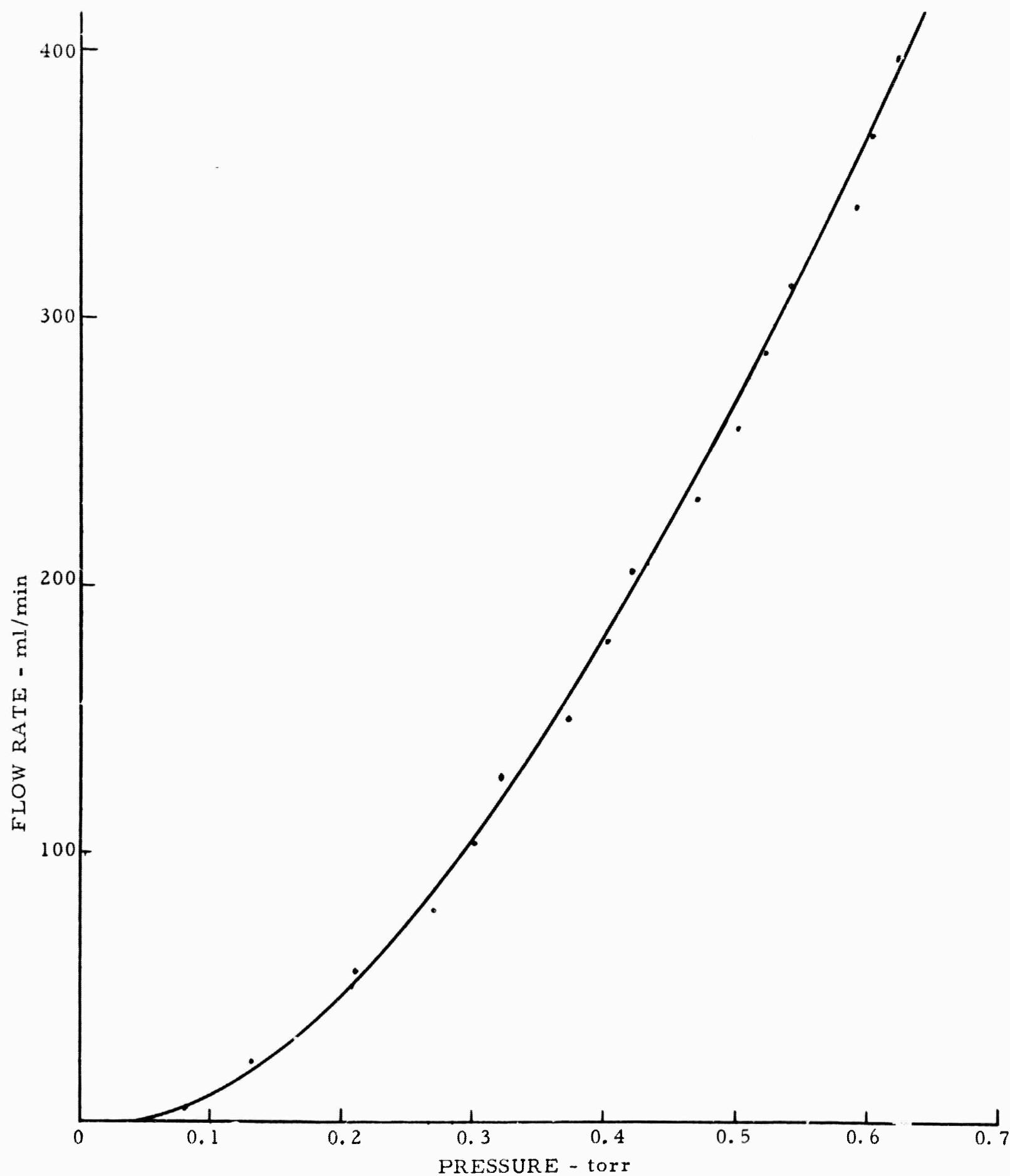
Figure 6.   Flow rate vs. pressure of cryogenic pump using Manostat FM 1043B
roto-meter.   Evacuation pressure - 11 μ,   Final pressure - 50 μ.

pump was not approached. Flow rate measurements were made with a Manostat FM 1043B roto-meter using the steel ball. The pressure reached a constant value within a few seconds after adjusting the flow rates over the entire range. After the test with air flow into the system, the pump would evacuate the system to 5×10^{-2} torr.

The second test was to determine the air capacity of the pump at a particular flow rate of 287 ml/min. Figure 7 shows the results of this test. Initially, the pump was heated and evacuated to 10^{-2} torr pressure overnight. The plot of time versus pressure shows that for this flow rate the pressure may be kept below 1 torr until there is 36 liters of air in the pump. If the flow rate is then decreased, the pressure will decrease.

The third test was to determine the length of time that the pump could maintain a pressure at 10^{-1} torr. The flow rates reported here are characteristic of the system tube size and the bends. The flow rate to obtain 10^{-1} torr was 9.4 ml/min. Flow rate versus time at 10^{-1} torr was plotted for 4 1/2 hours. A test was also made at 5×10^{-2} torr with nitrogen. The system was maintained at this pressure for a minimum of 10 hours with a flow of 3.5 ml/min.
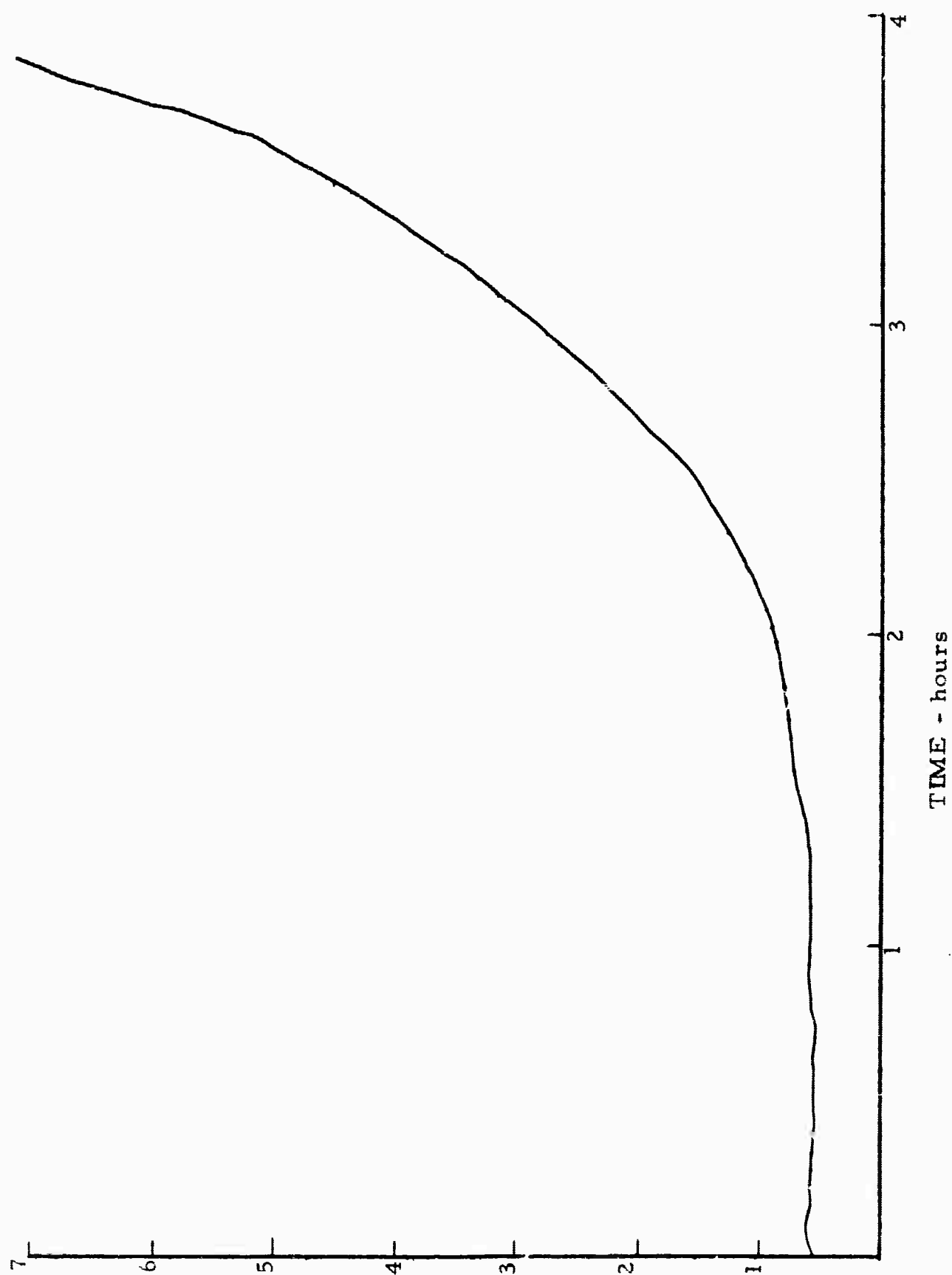
Figure 7. Flow rate vs. air capacity of cryogenic pump using Manostat FM 1043B roto-meter
Flow rate - 287 ml/min.

TIME - hours

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